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**EDGEWOOD ARSENAL  
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**SYMMETRY OF ABSORPTION AND EMISSION  
BAND SHAPES OF IMPURITIES IN SOLIDS**

by

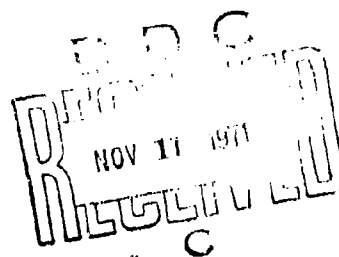
C. Stuart Kelley

October 1971



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## FOREWORD

The work described in this report was conducted under Project 1W562603A065, Flame, Incendiary, and Smoke Technology. The work was started in June and completed in July 1971.

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### DIGEST

Absorption and emission spectra of impurities in solids are calculated quantum mechanically; the lattice-impurity interaction is introduced by a configuration coordinate model. When the vibrational energies of the ground and excited states differ, the spectra are near mirror images at 0°K and virtually identical well above 0°K. The spacing of the emission transitions differs from that of the absorption transitions and the intensities are equal to those of the absorption spectrum at an effective temperature that involves the ratio of the excited state vibrational energy and the ground state vibrational energy.

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# SYMMETRY OF ABSORPTION AND EMISSION BAND SHAPES OF IMPURITIES IN SOLIDS

The absorption and emission spectra of an impurity in a solid consist of purely electronic transitions (zero phonon transitions, or those producing no change in the vibrational state of the lattice) and electronic transitions that occur simultaneously with changes in the vibrational state of the lattice (phonon assisted transitions).<sup>1-3</sup> At very low temperatures, the emission spectrum of the impurity can be regarded as the mirror image of the absorption spectrum. Using this aspect of the spectra, zero phonon transitions have been identified from among phonon assisted transitions.<sup>4,5</sup> The present article concerns the extent to which this mirror symmetry of the spectra occurs.

The impurity system is treated quantum mechanically by a configuration coordinate model in which the ground and excited states are harmonic oscillators having different vibrational frequencies. The minimum of the excited state is displaced from that of the ground state by the energy  $E_0$  and the configuration coordinate  $q_0$ . Matrix elements for transitions between vibrational levels of the ground and excited states have been derived.<sup>6</sup> For simplicity, the model considered here is for small  $q_0$ , a situation which appears to be applicable to at least one impurity system observed experimentally.\* Within the harmonic approximation, the matrix elements for transitions in this system<sup>7</sup> have been combined with appropriate Boltzmann factors to give the absorption spectrum:<sup>7</sup>

$$P_a(E,T) = C \langle \phi | e^{\vec{r}} | \phi' \rangle^2 \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} [2\sqrt{R(f!)/(1+R)(i!)}] \\ \left[ \frac{P_{(i-f)/2}}{P_{(i+f)/2}} [2\sqrt{R/(1+R)}] \right]^2 \left\{ \sum_{j=0}^{\infty} e^{(i-j)\theta/T} \right\}^{-1} \\ \delta[E - E_0 - \frac{1}{2}(R-1)\hbar\omega_i - (Rf-i)\hbar\omega_i]. \quad (1)$$

\* Kelley, C. S., and Williams, F. E. The Near Infrared Optical Absorption of ZnS: Cr. Submitted for publication in Physical Review (September 1971).

<sup>1</sup> Kelley, C. S., and Williams, F. E. Phys. Rev. B2, 3 (1970).

<sup>2</sup> Williams, F. E. J. Chem. Phys. 19, 457 (1951).

<sup>3</sup> Vallin, J. T., Slack, G. A., Roberts, S., and Hughes, A. E. Phys. Rev. B2, 4313 (1970).

<sup>4</sup> Ham, F. S., and Slack, G. A. Phys. Rev. B4, 777 (1971).

<sup>5</sup> Slack, G. A., and O'Meara, B. M. Phys. Rev. 163, 335 (1967).

<sup>6</sup> Kell, T. H. Phys. Rev. 140, A601 (1965).

<sup>7</sup> Kelley, C. S. EATR 4426. A Simplified Expression for Oscillator Strengths of Transitions Between Different Quadratic Modes of a Configuration Coordinate Model. August 1970. UNCLASSIFIED Report.

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The probability of absorption at the energy  $E$  and temperature  $T$  is  $P_a(E, T)$ , where  $C$  is a constant and  $\langle \phi | \vec{e} r | \phi' \rangle$  is the matrix element of the electronic dipole transition. The ratio of the excited state oscillator frequency  $\omega_f$  to that of the ground state  $\omega_i$  is  $R$ ;  $f$  and  $i$  are the quantum numbers of the excited and ground states. The functions  $P_p^H(x)$  are the associated Legendre polynomials. The delta functions indicate the location of the transitions, and the factors preceding them are the transition intensities. The selection rule for the transitions is that  $i+f$  must be even.

Because the wavefunctions are real, the matrix elements for emission are the same as those for absorption. Using the Boltzmann factor appropriate to the excited state, the probability of emission is

$$P_e(E, T) = C \langle \phi | \vec{e} r | \phi' \rangle^2 \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} [2\sqrt{R}(f!)/(1+R)(i!)] \left[ \frac{P_p^{(i-f)/2}(2\sqrt{R}/(1+R))}{P_p^{(i+f)/2}(2\sqrt{R}/(1+R))} \right]^2 \sum_{j=0}^{\infty} e^{-(f-j)R\theta/T} \delta \left[ E - E_0 - \frac{1}{2}(R-1)\hbar\omega_i - (Rf-i)\hbar\omega_i \right]. \quad (2)$$

It will be seen from equations 1 and 2 that the absorption and emission spectra are quite similar. The differences occur in: (1) the Boltzmann factors and (2) the spacings of the transitions.

The expressions for  $P_a$  and  $P_e$  at  $T = 0^\circ K$  simplify to

$$P_a(E, 0^\circ K) = C \langle \phi | \vec{e} r | \phi' \rangle^2 \frac{2\sqrt{R}}{(1+R)} \sum_{m=0}^{\infty} \frac{(2m)!}{4^m(m!)^2} \left( \frac{1-R}{1+R} \right)^{2m} \delta [E - E_{zp} - (2R\hbar\omega_i)m],$$

and

$$P_e(E, 0^\circ K) = C \langle \phi | \vec{e} r | \phi' \rangle^2 \frac{2\sqrt{R}}{(1+R)} \sum_{n=0}^{\infty} \frac{(2n)!}{4^n(n!)^2} \left( \frac{1-R}{1+R} \right)^{2n} \delta [E - E_{zp} + (2\hbar\omega_i)n],$$

where  $m = 2f$ ,  $n = 2i$ , and both can assume all positive integer values. The energy  $E_{zp} = E_0 + \frac{1}{2}(R-1)\hbar\omega_i$  locates the zero phonon transition.

The absorption and emission spectra at  $T = 0^\circ\text{K}$  for  $0 \leq m, n \leq 5$  are superposed in figure 1 for the case of  $R = 1.3$ . The ordinate is  $\log_{10} P'_a = \log_{10} P_a / C \langle \phi | e^{\vec{r}} | \phi \rangle^2$  and  $\log_{10} P'_e = \log_{10} P_e / C \langle \phi | e^{-\vec{r}} | \phi \rangle^2$ ; the abscissa is  $(E - E_{zp}) / 2\hbar\omega_f$ . The absorption spectrum, denoted  $i \rightarrow f$ , consists of those transitions on the high energy side of (and including) the  $0 \rightarrow 0$  transition. The emission spectrum, denoted  $f \leftarrow i$ , consists of those transitions on the low energy side of (and including) the  $0 \leftarrow 0$  transition. The intensities of corresponding absorption and emission lines are equal, a consequence of  $T = 0^\circ\text{K}$ . The zero phonon transition is common to both spectra and occurs at the overlap of the spectra. The mirror symmetry of the absorption and emission spectra is marred only by the spacing of the transitions. The spacing of the absorption transitions is 1.3 times that of the emission transitions, and, in general, at  $T = 0^\circ\text{K}$ , the ratio of the spacing of absorption transitions to the spacing of emission transitions is  $R$ .

This mirror symmetry is altered when  $T \neq 0^\circ\text{K}$ , as demonstrated in figures 2 and 3. These and subsequent figures were obtained through calculation of equations 1 and 2 by computer. The abscissas in these figures are  $Rf-i$ ; the ordinates are either  $P'_a$  or  $P'_e$ . As indicated by the figures, the dominant transitions at  $T = 0$  are for  $i \leftrightarrow f = i$ . There is no mirror symmetry, and the only difference in the absorption and emission spectra is that the emission spectrum may be regarded as the absorption spectrum at an effective temperature  $T_{\text{eff}} = T/R$  (refer to the Boltzmann factors in equations 1 and 2). Absorption and emission spectra at  $T = 110$  are shown in figures 4 and 5 and also illustrate this point.

The transition intensities cluster into groups characterized by  $i = f + 2k$ , where  $k = 0, 1, 2, \dots$  (see figures 2 through 5 and especially figures 4 and 5). The intensity of a particular transition is a balance between the overlap of the ground state and excited state wavefunctions (i.e., a small  $k$  produces a large overlap) and the Boltzmann factor (for absorption spectra at a specific temperature  $T$ , a small  $i$  produces a large line intensity). Because the most intense lines at  $T \gg 0^\circ\text{K}$  are those for which  $i = f$ , the transition intensity is more highly dependent on  $k$  than on the Boltzmann factor.

The above statements regarding the lack of mirror symmetry are unchanged if  $R < 1$ ; that is, if the excited state vibrational levels are more closely spaced than those of the ground state. For  $R < 1$ , the spectra appear to be rotated about the zero phonon transition from the  $R > 1$  spectra, the intensities and spacings of the transitions reflecting the change in  $R$ . This rotation of the spectra is due to the factor  $(Rf-i)\hbar\omega_f$  in the delta functions of equations 1 and 2. For both  $R > 1$  and  $R < 1$ , the spectra display clustering by  $k$  values. For  $R = 1$ , both the absorption and emission spectra consist of a single delta function located at  $E = E_0$ . This occurs because the only transitions are from  $i$  to  $f = i$ .

From the absorption (or emission) spectrum at  $T = 0^\circ\text{K}$ , the separation in energy of the zero and first phonon assisted transitions,  $R\hbar\omega_f$ , and the ratio of their intensities,  $(1-R)^2/2(1+R)^2$ , can be used to determine  $R$  and  $\omega_f$  and thereby  $\omega_g$ .

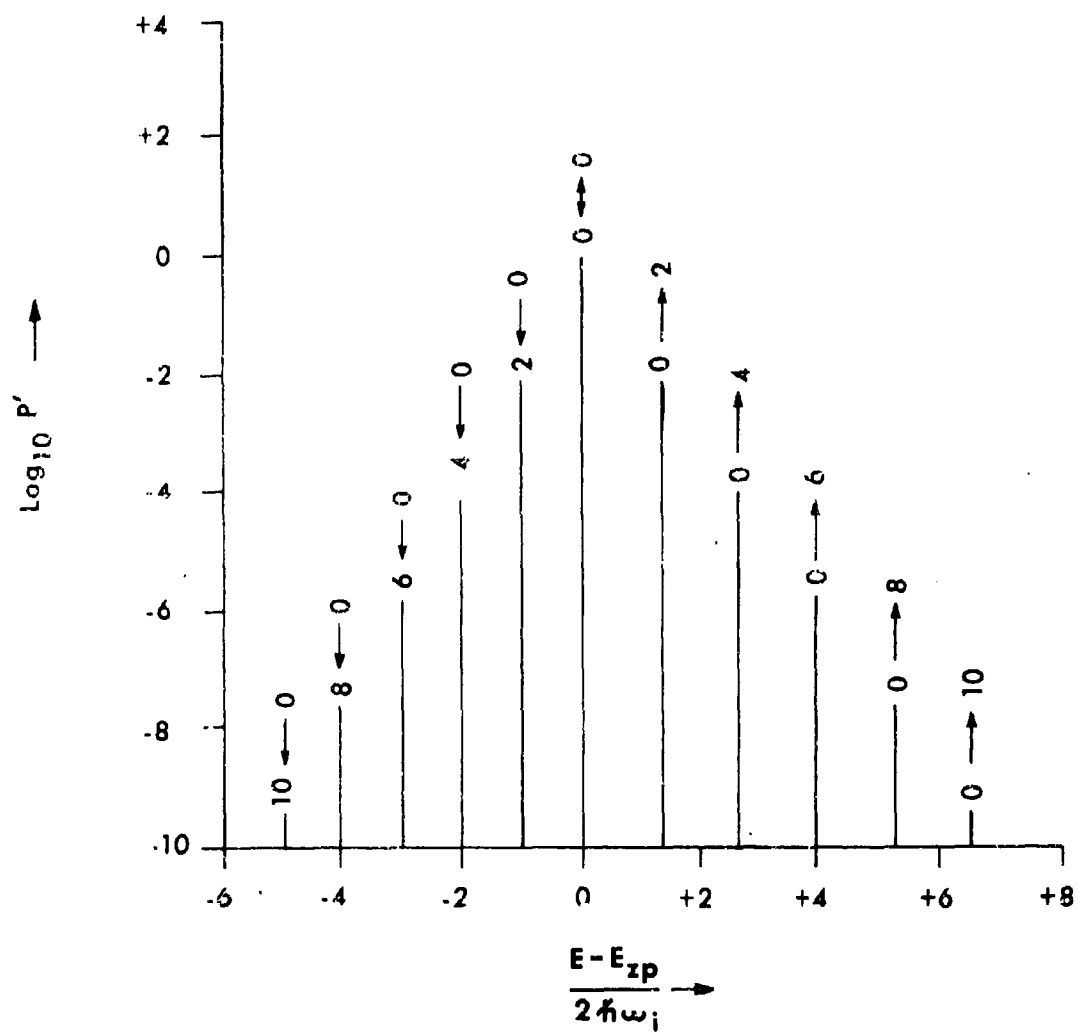


Figure 1. Absorption ( $i \rightarrow f$ ) and Emission ( $i \leftarrow f$ ) Spectra at  $0^\circ\text{K}$ , Illustrating the Near Mirror Symmetry of the Spectra

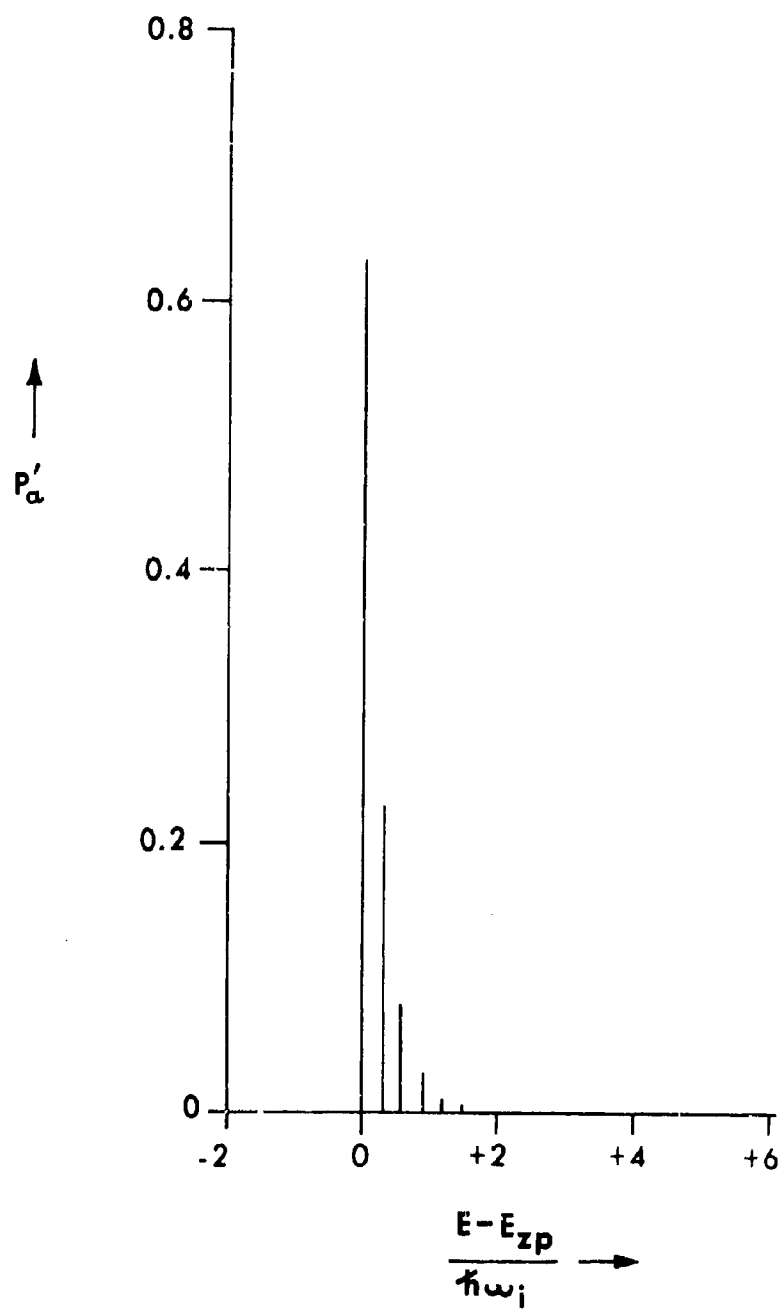


Figure 2. Absorption Spectrum at  $T = \theta$  for  $R = 1.3$

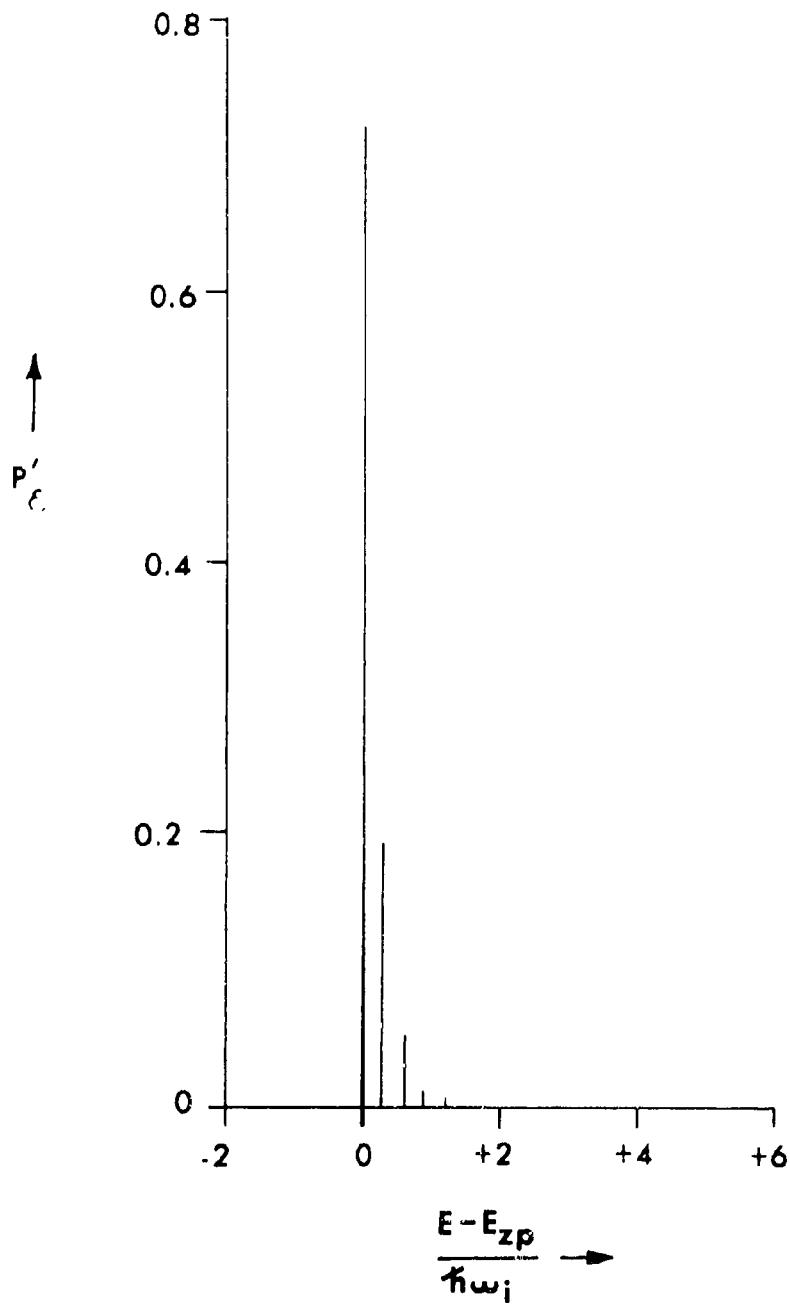


Figure 3. Emission Spectrum at  $T = 0$  for  $R = 1.3$

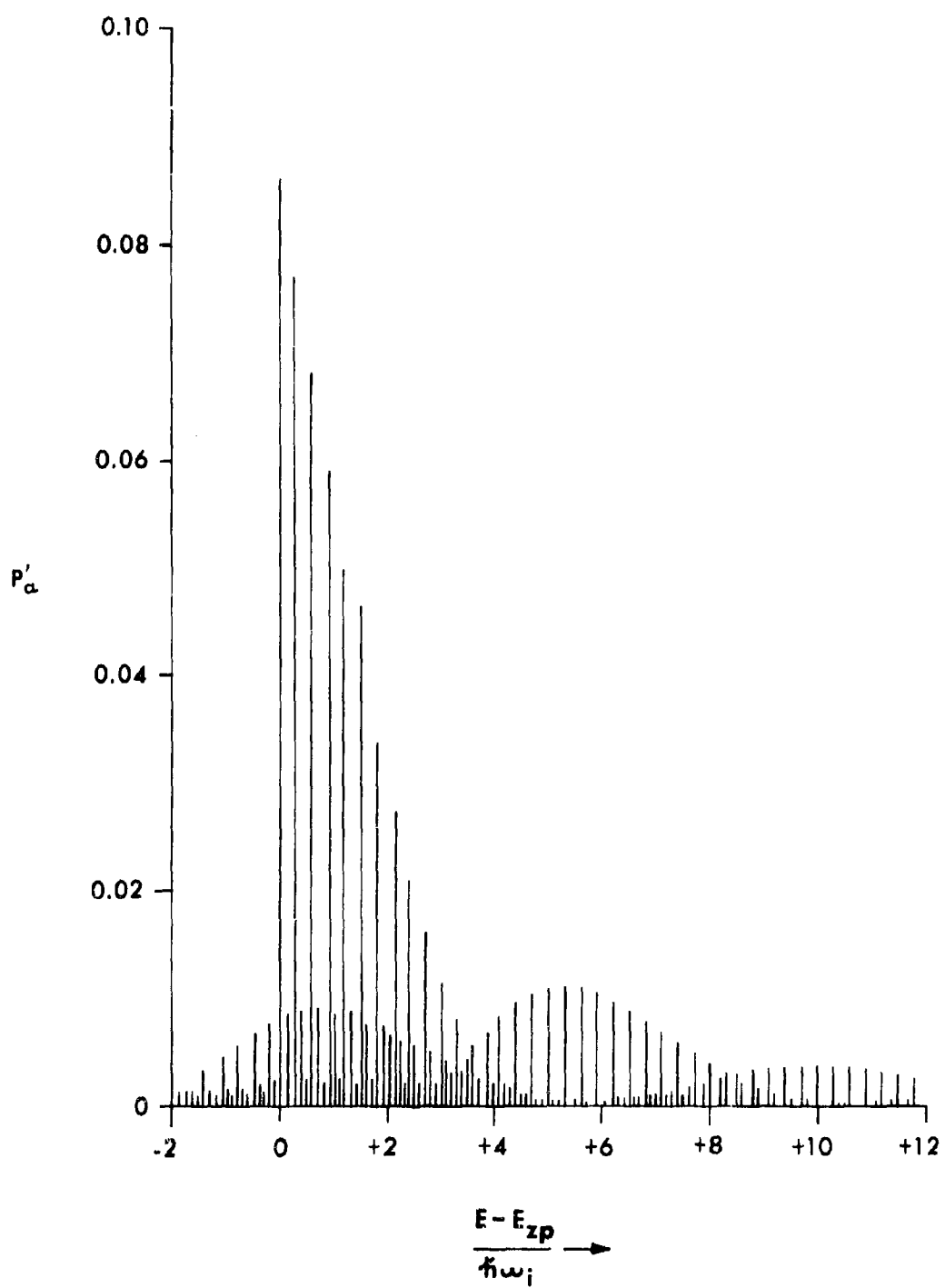


Figure 4. Absorption Spectrum at  $T = 11\theta$  for  $R = 1.3$

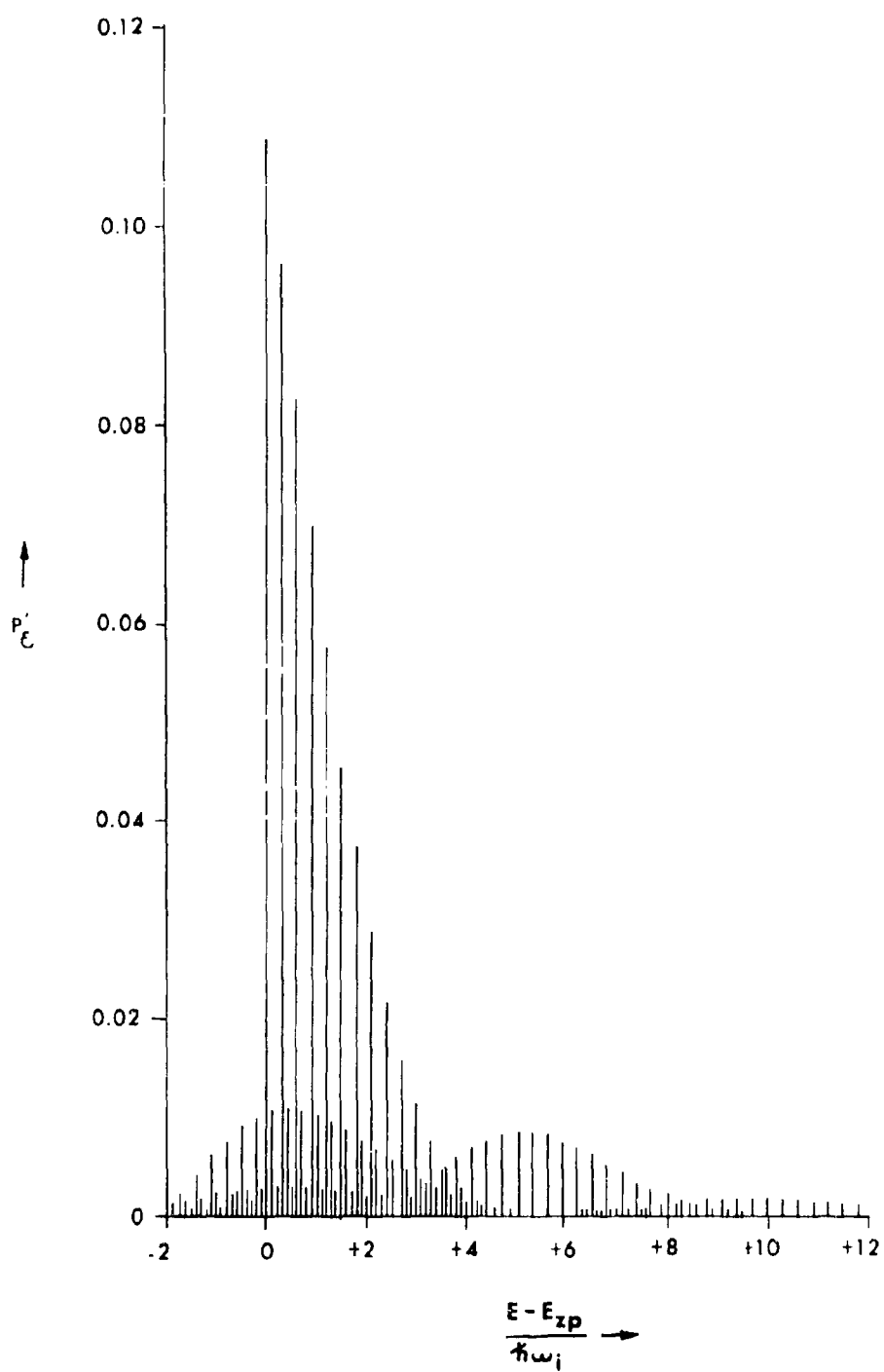


Figure 5. Emission Spectrum at  $T = 110$  for  $R = 1.3$

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